F-04-7

Reprinted from

Canadian Journal of Fisheries and Aquatic Sciences

Réimpression du

Journal canadien des sciences halieutiques et aquatiques

Downstream effects of mine effluent on an intermontane riparian system

J. N. Moore, S. N. Luoma, and D. Peters

Volume 48 • Number 2 • 1991

Pages 222–232

Printed in Canada by The Runge Press Limited
Imprimé au Canada par The Runge Press Limited

Downstream Effects of Mine Effluent on an Intermontane Riparian System

Johnnie N. Moore

Department of Geology, University of Montana, Missoula, MT 59812, USA

Samuel N. Luoma

U.S. Geological Survey, Water Resource Division, 345 Middlefield Road, Menlo Park, CA 94025, USA

and Donald Peters

Montana Department of Fish, Wildlife and Parks, 3201 Spurgin Road, Missoula, MT 59801, USA

Moore, J. N., S. N. Luoma, and D. Peters. 1991. Downstream effects of mine effluent on an intermontane riparian system. Can. J. Fish. Aquat. Sci. 48: 222–232.

Metal concentrations were determined in benthic biota, fish livers, water, and fine-grained sediment through 215 km of an intermontane river system (Blackfoot River, Montana, USA) affected by headwater inputs of acid-mine effluent. Solute and particulate contaminants decreased rapidly downstream from headwater sources, but some extended through an extensive marsh system. Particulate contaminants penetrated through the marsh system, effectively resulting in food web contamination downstream of the marshes. Metals differed in their bioavailability within and below the marsh system. Cadmium was most consistently accumulated in the food web, and the general order of downstream mobilization of bioavailable metals appears to be Cd, Zn > Cu > As, Ni. Depauperate benthic communities and reduced fish populations occurred coincident with the sediment contamination.

Les concentrations de métaux ont été déterminées sur 215 km dans le benthos, des foies de poisson, l'eau et les sédiments fins d'un bassin hydrographique intramontagneux (rivière Blackfoot, Montana, É.-U.) touché par des effluents acides de mine déversés à la source de ce bassin. Les concentrations de contaminants en solution ou particulaires allaient en décroissant rapidement des eaux de tête vers l'aval, mais une certaine part de ces contaminants s'est répandue dans un important réseau de marais. Les contaminants particulaires ont pénétré dans le réseau de marais et ont contaminé le réseau alimentaire en aval des marais. La biodisponibilité des métaux variaient tant dans les marais qu'en aval de ces derniers. Le cadmium est le métal le plus abondamment retrouvé dans le réseau alimentaire; en aval, l'importance relative de la contamination effective par ces métaux biodisponibles suivait l'ordre suivant : Cd, Zn > Cu > As, Ni. La contamination des sédiments était corrélée à un appauvrissement des communautés benthiques et à une réduction des populations de poisson.

Received March 30, 1989
Accepted August 20, 1990
(JA115)

Reçu le 30 mars 1989
Accepté le 20 août 1990

As water supplies are stressed, there is concern over the effects and extent of metal contamination in the headwaters of drainage basins in western North America from past hard-rock mining activities (NOVA 1990). However, systematic studies of downstream sediment contamination and subsequent availability to biota of metals mobilized by acid-mine drainage are rare. Many studies of metal-contaminated riparian systems have focused on only a few kilometres of river near the input of contaminants (Moraiarity et al. 1982; Bradley and Cox 1987) and do not integrate contamination in the solid and aqueous phases with the biological system. As well, metal bioavailability in cobble bed rivers is poorly understood in general, partly because the biological communities of such systems are complex and difficult to sample. In this paper, we present data showing that headwater inputs of aqueous and particulate metal contaminants into a cobble bed river can affect chemical trends, metal concentrations, and metal bioavailability over a distance of tens of kilometres from the source. The goal is to understand the biological fate of metals mobilized by acid mine drainage, and specifically address the following questions: (1) Are high concentrations of metals near inputs of mine effluent available to resident biota? (2) Do beaver ponds/marsh systems (often characteristic of headwater streams) mitigate contaminant transfer downstream? (3) If metals are trapped in such a marsh system, do they remain available to resident biota? (4) How does spatial distribution of contamination in food webs compare with the particulate and aqueous phases of contamination? (5) Does contaminant bioavailability differ among metals or taxa? (6) Does metal bioavailability vary substantially from year to year?

Six taxa of benthic insect larvae, from two trophic levels, and three taxa of trout were sampled as representatives of the food web in a river system in western Montana (the Blackfoot River) contaminated by headwater inputs of mine effluents (acid mine drainage). Metal concentrations (Al, Cd, Cu, Fe, Pb, and Zn plus the metalloid As) were determined in whole bodies of benthic biota, fish livers, water, and fine-grained sediment. Metal contamination in benthic insects was compared with particulate and aqueous contamination, and contamination trends compared with distribution of fish populations in the

river. To assess the area of contaminant distribution, the complete river system was examined from the headwaters to its mouth, 215 km downstream, including inputs from all mine effluent sources. Comparisons were made with earlier studies conducted during 1971–75 (Spence 1975) to determine the temporal changes in the system.

Study Area

The Blackfoot River of western Montana is a Class I trout stream (Montana Department of Fish, Wildlife and Parks classification system) dissecting geologically complex, mineralized terrains of the northern Rocky Mountains. The river drains 6000 km^2, and from its source near the Continental Divide flows 215 km where it joins the Clark Fork River (Fig. 1). Mining in the headwaters of the Blackfoot River began in approximately 1865 and continued until after World War II. A variety of minerals and commodities were recovered including gold, silver, lead, and copper from numerous small placer and hardrock mining operations. Although milling was not widespread in the drainage, milled tailings were discharged into the headwaters at several sites. The numerous small deposits of contaminated tailings and isolated sources of contaminated mine drainage in the upper reaches of the catchment (Fig. 1; Spence 1975) are typical of many montane areas in western North America.

The gradient of the Blackfoot River ranges from 0.5 to 60 m/km and is characterized by distinct changes in slope. The stairstep nature of the stream profile results from deposition of glacial deposits during the Pleistocene at the mouths of several tributaries, producing low-gradient reaches separated by higher gradient sections. Tributaries in the headwaters which drain the mining areas have relatively high gradients. Downstream from the mined areas, the river valley has been partially dammed by Pleistocene glacial till and outwash to form several low-gradient reaches. One such reach, extending from 211.6 to 196.6 km, has three extensive marshes (river kilometres are measured from the mouth upstream).

Earlier studies (Spence 1975) showed that acid-mine drainage caused enrichment in sulfate and metals (including Al, Cd, Ca, Cu, Pb, Mn, and Zn) in Blackfoot water downstream to approximately 190 km. Waters flowing from tunnels and bore holes were commonly of pH < 3 and no fish were found in tributaries affected by this acidic drainage (Spence 1975; Dollhopf et al. 1988). Drainage from adits and waste piles continue to supply contaminated water to the headwaters of the drainage. Spence found that bed sediment in the upper Blackfoot River was especially enriched with Cd, Cu, and Zn and that the bed was coated with Fe–Mn oxyhydroxide for several kilometres. This contamination is still visually and chemically evident today. In the early 1970's, marshes along the upper river appeared to impede downstream movement of the metals, as shown by reductions in contamination below the uppermost wetland (Spence 1975). Thus the stream morphology established a natural mitigation process that appeared to limit downstream dispersion of mine effluents.

The benthic community in much of the Blackfoot River is a diverse assemblage of insect larvae typical of temperate, cobble bed rivers (Spence 1975). The trout fishery is a complex, multispecies assemblage (Spence 1975; Peters and Spoon 1989). In general, eastern brook trout (*Salvelinus fontinalis*) and cutthroat trout (*Oncorhynchus clarki lewisi*) are the dominant species from the headwaters to approximately 191.5 km. A transition zone occurs below 190 km to 168.5 km where brown trout (*Salmo trutta*) dominate the assemblage. Brown trout are replaced by rainbow trout (*Oncorhynchus mykiss*) in the lower river (below 85 km). Large, fluvial bull trout (*Salvelinus confluentus*) also are found in the middle and lower river. The trout fishery is an important recreational resource in western Montana.

Methods

Water Chemistry

Grab samples of river water were taken at 22 sites on the main stem, 9 on tributaries and 9 from contaminated tributaries

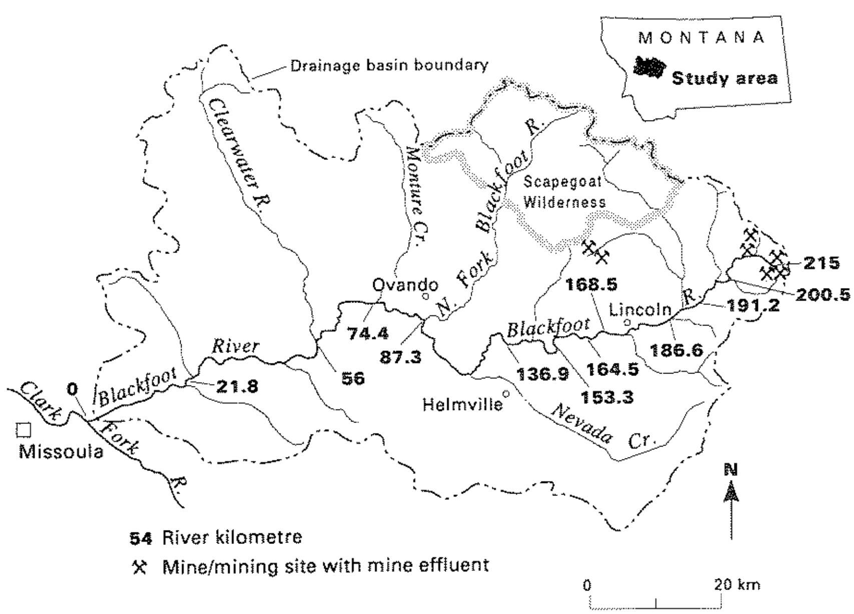

FIG. 1. Map of the Blackfoot River drainage basin, with biological sampling locations designated by kilometre from the mouth of the river.

(those tributaries with known mine effluent input). One sample from each location was filtered in the field through a 0.45-μm nucleopore membrane filter that was first rinsed with river water. The filtered sample was preserved for metal analyses by acidifying with concentrated, "instra-analyzed" nitric acid. Metal analyses were performed by inductively coupled argon plasma spectrometry (ICAPES). Detection limits are listed in Table 1. Another filtered sample was left unacidified for anion analysis by ion chromatography (IC). A third water sample was left unfiltered and unacidified for alkalinity measurement by titration (Gran method). All samples were transported to the laboratory on ice and refrigerated until analysis. Quality control during ICAPES analysis was maintained by using field and procedural blanks and U.S. Geological Survey water standards (Table 1). IC analyses were checked using internal standards.

Sediment Chemistry

Sediment samples were taken at 43 sites on the main stem, tributaries, and contaminated tributaries. Eight sites were replicated in 1988 and 1989 to determine annual variation (which was within the error of measurement). Surficial bed sediment was collected by suction in a large syringe (a turkey baster) from small deposits of fine-grained sediment over an area of 50 to 100 m^2 and composited by sieving through a 63-μm nylon screen. The resulting slurry was stored on ice, transported to the laboratory, centrifuged, and dried at 70°C. Dried sediment (0.2 g) was dissolved in a microwave digestion vessel in 5 mL of aqua regia and 2 mL of HF. After microwaving for 5 min at high power, the sample was filtered and the HF neutralized with boric acid. Then the sample was diluted 500:1 (v/w) and analyzed by ICAPES. Quality control was evaluated by using NBS sediment standards (Table 1).

Benthic Insect Larvae

Samples of benthic insect larvae were collected for metal analysis from 13 different stations in 1987, 1988, and 1989. Four stations were sampled between 190 and 17 km in 1987 and eight stations through that reach in 1988. Stations between 211.8 and 186.6 km (including 190 km) were sampled from riffles within and below the marsh system in 1989. The six taxa targeted for collection were relatively abundant, larger insect larvae from three functional groups. These included two predaceous Plecoptera (stoneflies), *Claassenia sabulosa* and *Hesperoperla pacifica* (family Perlidae), and four Trichoptera (caddisflies), the net-spinners *Hydropsyche* sp. and *Arctopsyche grandis* (family Hydropsychidae), the herbivore *Brachycentrus* sp. (family Brachycentridae), and the large case-bearing scavenger *Limnophilus* sp. *Brachycentrus, Limnophilus,* and *Hydropsyche* samples were not separated to species. Metal concentrations among species of *Hydropsyche* do not differ greatly in other systems (Cain et al. 1989).

The larvae were collected by kick net from rifle areas. For reference, metal concentrations from the Blackfoot taxa were compared with animals from Rock Creek, an undisturbed stream located in an adjacent drainage (Luoma et al. 1989; Axtmann et al. 1990). Taxa were separated for analysis and brachycentrids and limnophilids were removed from their cases in the field. Living animals were held for 4 to 6 h in bags of ambient water after separation for cleansing of their digestive tracts before the samples were frozen. In preparation for analyzes, frozen samples were thawed, the length of individuals from the larger taxa (*Claassenia* and *Hesperoperla*) was determined, and similar sized individuals were composited to a dry weight of at least 50 mg, but not more than 1.5 g. Microscopic verification of field taxonomy was conducted where necessary

TABLE 1. Concentrations (and standard deviations) for U.S. Geological Survey (USGS) water standards, National Bureau of Standards (NBS) sediment standard, and NBS bovine liver standard. Limits of detection (LOD) listed for solution only. All values listed in parts per million (ppm) for solids and mg/L for solutions, except where in weight % which is identified by an asterisk. NC = noncertified value; BD = below detection limit.

		Water standards				Sediment standard NBS 1645		Bovine liver NBS 1577a	
		USGS T103		USGS T97					
Metal	LOD	Given	Obtained ($n=6$)	Given	Obtained ($n=6$)	Given	Obtained ($n=4$)	Given	Obtained ($n=6$)
Al	0.03	0.127 (0.038)	0.136 (0.006)	0.126 (0.042)	0.156 (0.007)	2.26 (0.04)*	2.29 (0.09)*	2 (NC)	3.02 (0.51)
As	0.05	0.032 (0.0009)	BD	0.0113 (0.0015)	BD	66 (NC)	63 (8.4)	0.047 (0.006)	BD
Cd	0.005	0.0017 (0.0004)	0.002 (0.001)	0.0163 (0.0023)	0.016 (0.002)	10.2 (1.5)	6.7 (0.5)	0.44 (0.06)	0.37 (0.02)
Cu	0.005	0.0833 (0.0057)	0.082 (0.005)	0.0168 (0.0025)	0.015 (0.003)	109 (19)	101 (2.3)	158 (7)	155 (0.98)
Fe	0.005	0.041 (0.0076)	0.039 (0.002)	0.100 (0.009)	0.105 (0.004)	11.3 (1.2)*	9.16 (0.28)*	194 (20)	187 (3.5)
Mn	0.005	0.009 (0.0021)	0.007 (0.001)	0.0305 (0.0032)	0.029 (0.001)	785 (97)	695 (15)	9.9 (0.8)	9.95 (0.11)
Pb	0.04	0.0077 (0.0021)	BD	0.015 (0.0037)	BD	714 (28)	614 (16)	0.135 (0.015)	BD
Zn	0.005	0.0265 (0.0041)	0.033 (0.002)	0.153 (0.01)	0.159 (0.006)	1720 (170)	1525 (37)	123 (8)	127 (0.6)

on frozen samples. Each composite was digested by concentrated nitric acid reflux, the concentrated acid was evaporated, and the sample was reconstituted in 0.5 N HCl. Metal analyses in 1987 were conducted by flame atomic absorption spectrophotometry. Analyses in 1988 and 1989 were conducted by ICAPES.

The goal of benthic insect larvae collection at each site was to obtain at least 20 individuals of each available taxon with sufficient mass of each to exceed analytical detection limits. Achieving these goals for a variety of taxa in cobble bed rivers is made difficult by the spatial, temporal, and size variability typical of the benthic community (Giesey et al. 1981; Selby et al. 1985). As a result, more individuals of some taxa were collected than others at each station, the number of composites that represented an individual taxon at a site varied, and not all taxa were represented at all stations. Where more than one composite of a taxon was collected, confidence intervals were calculated to illustrate within-site variability. Data from adjacent sites also were aggregated in some cases to eliminate pseudoreplication and to test if differences between segments of the river were statistically different. Differences between segments or stations were tested by one-way ANOVA or by *t*-test. Data were log-transformed for statistical comparisons.

Fish

Fish were collected for metal analyses in 1988 and 1989. The metals of principal concern in the Blackfoot (Cd, Cu, and Zn) typically concentrate strongly in the liver (Bollingberg and Johansen 1979; Wiener and Giesy 1979). Thus, analyses of this organ were employed to determine the distribution of metal contamination of the Blackfoot fishery, as proven effective elsewhere (Roch et al. 1982). All comparisons of metal concentrations were restricted to similar size classes of fish within a species (Brooks et al. 1976; Chernoff and Dooley 1979). To compare contamination in the upper Blackfoot with a reference, cutthroat trout also were collected from Marshall Creek, a small stream undisturbed by mining near the Blackfoot River, but not in the drainage (not on Fig. 1). All fish were collected by electrofishing from river reaches exceeding 1 km long and immediately placed on ice. The length of each individual fish was measured and the liver removed for analysis within 6 h of collection. Liver samples were digested by the concentrated nitric acid reflux method described above and analyzed by ICAPES. NBS standard 1577a (bovine liver) was analyzed by the same method (Table 1). All statistical comparisons employed one-way ANOVA with log-transformed data.

Fish populations were estimated with the mark and recapture method, employing Chapman's modification of the Peterson formula described by Ricker (1975). Variance estimates were made with Chapman's formula (Ricker 1975). These methods were employed to provide direct comparison with a similar approach employed in earlier fish surveys in the Blackfoot (Spence 1975). Similar habitat was sampled from all sections that were compared. Detailed methods and a complete discussion of the fish population survey are available in Peters and Spoon (1989). Data from all biological and sediment metal analyses are available in Moore (1990).

Results

Solute Contaminants

The water in the lower main stem of the river (below 190 km) and in uncontaminated tributaries is a Ca–Mg–HCO_3 type low

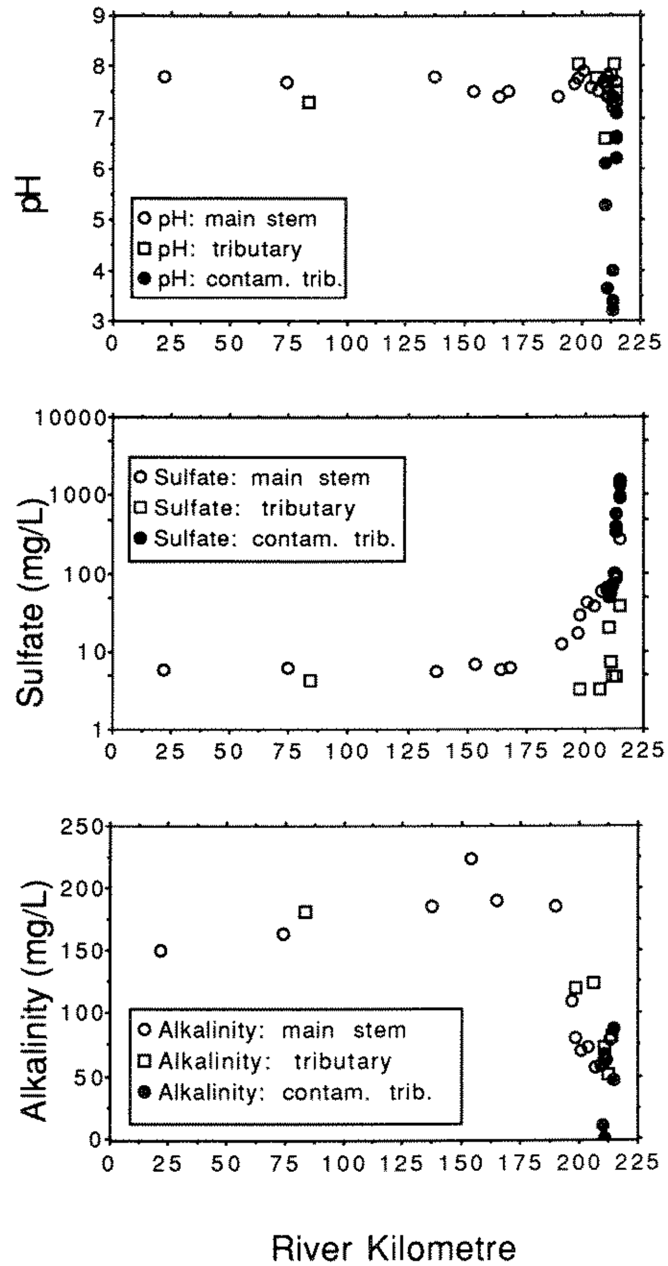

FIG. 2. Plots of pH, sulfate, and alkalinity ($CaCO_3$) vs. river kilometre. Tributaries and contaminated tributaries are plotted at the kilometre where they join the main stem of the Backfoot River. Contaminated tributaries have known mine effluent inputs; tributaries have no known mining inputs.

in sulfate, nitrate, fluoride, and trace constituents with pH's from 7.4 to 8.0. Contaminant input from mine effluent in the headwaters into the Blackfoot River is apparent from downstream trends of solute constituents. The pH of contaminated tributaries that flow into the upper 5 km of the river (mostly above the upper marsh system, but two contaminated tributaries flow directly into the upper marsh) ranges from 3 to 6.5 (Fig. 2). Concentrations of sulfate are extremely high in the acidic tributaries (Fig. 2) and decrease downstream away from input.

Both acidity and sulfate concentration show downstream attenuation from the headwater sources in the Blackfoot River. Acidity is neutralized rapidly and pH reaches background (uncontaminated tributary and downstream mainstem) values before reaching the marsh system (211.6 km). Sulfate, however, shows less attenuation and penetrates downstream through the marshes; values above background extend to 190 km. Alkalinity of some mine effluent is near zero, but alkalinity of main stem and tributary water ranges from 50 to 100 mg $CaCO_3$ (including contaminated tributaries). Alkalinity generally increases downstream (Fig. 2).

Trends of Cd, Cu, and Pb in water show minimal injection of contaminants downstream from the sources (Fig. 3; As was below detection limit, 0.050 mg/L, for all samples exept in two mine effluents, as was Ni; other elements analyzed are not plotted). Concentrations of these elements decrease to values not detectably different from uncontaminated tributaries (mostly below detection limit) within the upper few kilometres of river. Iron, Mn, and Zn show more intrusion downstream (Fig. 3), but nearly all solute components reach detection limits 25 km downstream. Only Zn shows irregularities from this trend (possibly resulting from sample contamination).

These trends show that although most solute trace metals (Al, Cd, Cu, Mn, Ni, and Pb) are elevated from one to three orders of magnitude levels in the contaminated tributaries and the upper few kilometres of river, they decrease to levels of detection before entering the marsh systems at 211.5. Sulfate, Fe, Mn, and Zn are detectable farther downstream, into and through the upper marsh.

Total effluent input, from all adits and tunnels (all above 210 km) during low flows, accounts for approximately 7 to 14% of total river flow at 207 km (Spence 1975). Although there are several sources for the contaminants, one adit supplies most of the flow into the headwaters. Approximately 80% of

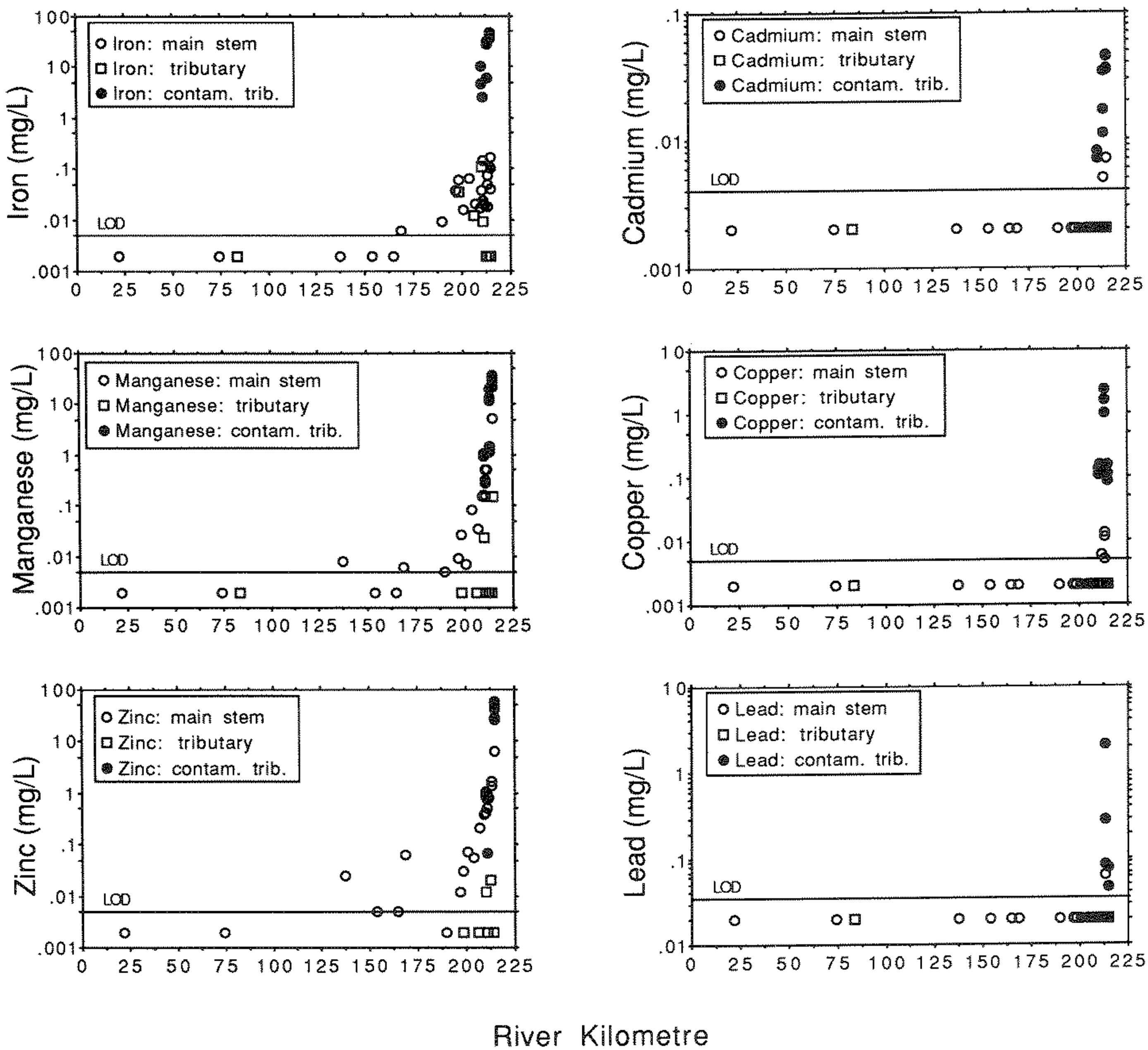

FIG. 3. Concentrations of Fe, Mn, Zn, Cd, Cu, and Pb in Blackfoot River water vs. river kilometre. Tributaries and contaminated tributaries are plotted at the kilometre where they join the main stem of the Blackfoot River. Contaminated tributaries have known mine effluent inputs; tributaries have no known mining inputs.

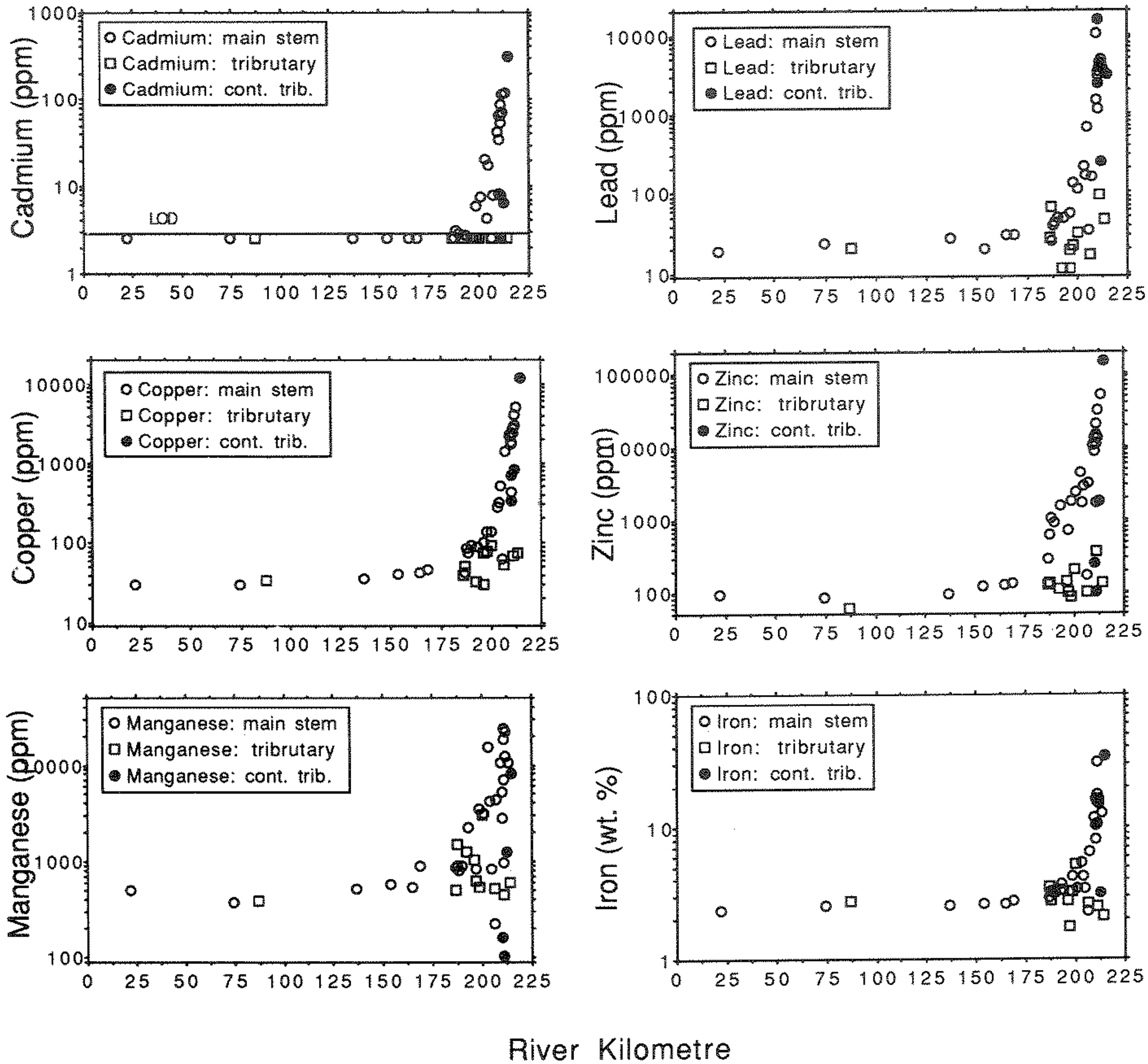

FIG. 4. Concentrations of Cd, Cu, Mn, Pb, Zn, and Fe in Blackfoot River bed sediment vs. river kilometre. Tributaries and contaminated tributaries are plotted at the kilometre where they join the main stem of the Blackfoot River. Contaminated tributaries have known mine effluent inputs; tributaries have no known mining inputs.

the mine effluent comes from that one mine at the farthest upstream (215.1 km) input (Spence 1975). These inputs are possibly diluted at high flows but no measurements have been made on mine inputs during spring runoff.

Sediment Contaminants

Compositional characteristics are distinctly different and concentrations of the trace elements As, Cd, Cu, Mn, Ni, Pb, and Zn are 10 to 1000 times higher in bed sediments in the upper few kilometres of the Blackfoot River compared with uncontaminated tributaries (background values) or sediment downstream (Fig. 4; As is only high in the uppermost reaches of the river and Ni is less enriched than all other metals, so these are not plotted). Solute and sediment contamination have similar sources. The sediment contamination originates from a small number of headwater tributaries and the major input of mine effluent at 215.1 km in the headwater mainstem. Concentrations of metals in sediments decrease rapidly downstream. It is unclear from these trends how much of the decrease is the result of downstream dilution of contaminants by uncontaminated sediment from tributaries, and how much is due to the action of the marshes. Trends through the marshes were complex and details differed from metal to metal. Figure 5 demonstrates that sediments 10 km beyond the marsh system (at 190 km) were substantially contaminated with metals such as Cu and Zn, compared with farther downstream.

Iron follows the trend of the trace elements (Fig. 4), higher-than-background concentrations penetrating downstream approximately 25 km from the main sources. In contrast, Al,

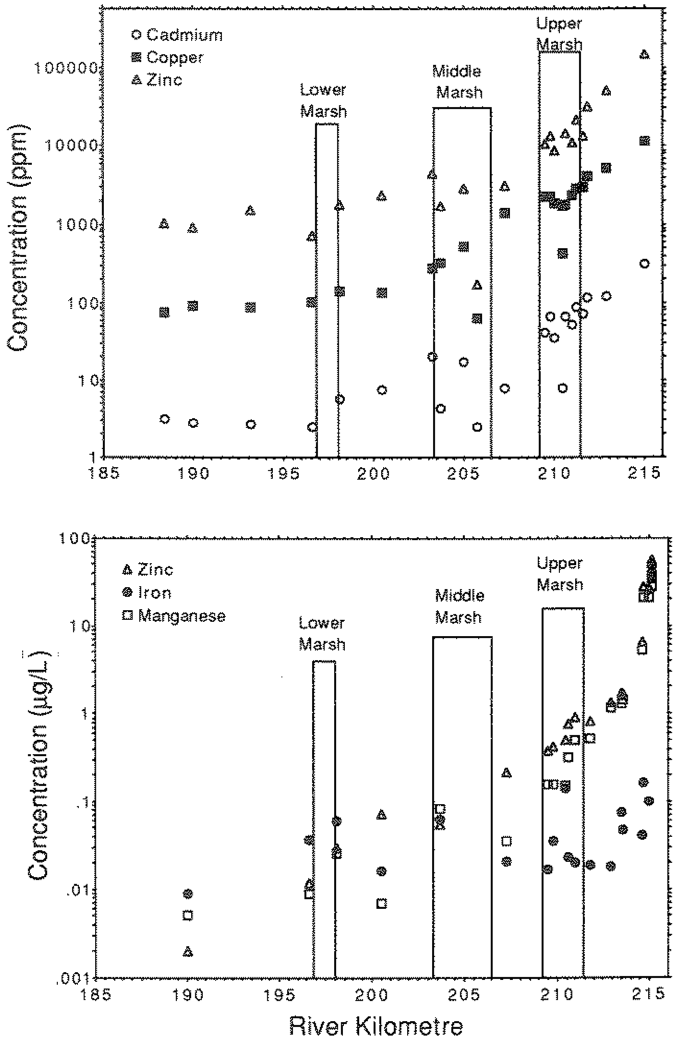

FIG. 5. Trends in concentrations of representative metals in sediments (upper) and water (lower) through the marsh systems in the upper Blackfoot River. Blocks indicate the locations of marshes.

Ca, and Ti were depleted in the headwaters and then increased rapidly downstream to values similar to most tributary and downstream sediments (data in Moore 1990).

In the upper few kilometres of river it is visually apparent that contaminated sediment is associated with Fe–Mn oxyhydroxides. All contaminated tributaries and the upper main stem have beds coated with red–orange oxyhydroxide precipitates. As acid mine drainage flows from the subsurface into the oxygenated surface waters, oxyhydroxides precipitate from solution, along with other hydroxide and sulfate minerals (Nordstrom 1982). These oxyhydroxides act as a source for particulate contamination downstream (Jones 1986; Filipek et al. 1987; Nordstrom 1982).

Metals in Biota

A qualitative estimation of presence/absence of targeted benthic fauna and mayflies (a metal-sensitive order, Winner et al. 1980) indicated that important faunal groups were absent where sediment was most contaminated. No benthic biota were found at 211.8 km where rocks were obviously coated with Fe–Mn oxyhydroxides. Limnophilids were the only targeted benthos found at 207 km. The communities at 101 and 190 km also were missing taxa typical of such streams. For example,

TABLE 2. Year-to-year differences of Cd concentrations (µg/g dry weight) at three stations in the Blackfoot River in two types of insect larvae and cutthroat trout. Caddisfly is *Arctopsyche grandis*. Data for *Hesperoperla pacifica* and *Claassenia sabulosa* are combined to obtain stonefly comparison. NC = not collected; NP = not present.

Kilometre	Year	Caddisfly	Stonefly	Cutthroat trout
21.8	1987	<0.2	0.12	
	1988	0.30	0.10	
	1989	0.16	0.08	
74.4	1987	0.20	0.20	
	1987	0.18	0.09	
190	1987	NC	1.30	NC
	1988	3.27	NP	0.61 ± 0.21
	1989	1.26	0.76	0.60 ± 0.08

hydropsychid caddisflies and mayflies were absent at 200.5 km in 1989. Absent groups at 190 km included hydropsychid caddisflies in 1988 and 1989, perlid stoneflies in 1988, and mayflies at least in 1989 (the only year the search included mayflies). Hydropsychids, perlids, and mayflies were present at 186.6 km and all other downstream stations.

Downstream trends in metal concentrations in the food web of the river were similar in the three surveys. Year-to-year variability at three stations are exemplified for Cd in three taxa in Table 2 (all data in Moore 1990). Because of the general agreement among years, data from 1987, 1988, and 1989 were aggregated to summarize spatial distributions in the following analysis.

Metals differed from one another in their bioavailability within and below the marsh system. Cadmium was the element most consistently accumulated throughout the food web. It was significantly enriched ($p < 0.01$) in caddisflies, stoneflies, and brook trout collected from within the marsh system, when compared with downstream segments of the river (Tables 3 and 4). Although only two cutthroat trout were found in the marsh collections, their livers contained concentrations of Cd more than 30 times higher than found at the reference site. Significant Cd enrichment also appeared throughout the food web at 190 km, downstream from the marsh sytem, suggesting that the Cd contamination in sediments that penetrated through the marshes was bioavailable. Cadmium concentrations in caddisflies, stoneflies, and both species of trout were significantly higher at 190 km than in the middle (137 to 168 km) and lower (17 to 87 km) segments of the river (Tables 3 and 4). Cutthroat trout contained 3.3 times more Cd at 190 km than in the reference area ($p < 0.01$).

Bioavailable Cd contamination appeared to extend to the middle reaches of the river. Cadmium concentrations in caddisflies were not significantly different between the middle and lower segments of the river, as observed in sediments (Table 3). However, in stoneflies and in large brown trout, significant ($p < 0.05$ for insects; $p < 0.01$ for brown trout) Cd contamination was observed in the middle reach compared with the lower reach (Tables 3 and 5). The longer life and/or predaceous nature of these two groups appeared to make them sensitive indicators of Cd contamination.

Significant ($p < 0.01$) Zn contamination of the food web also extended downstream through the middle reach of the river as observed in *Brachycentrus*, *Arctopsyche*, and *Hesperoperla* (see Moore 1990 for data). Concentrations of Zn in brook trout livers were enriched significantly within, but not below, the

TABLE 3. Spatial distribution of Cd (μg/g dry weight ± 1 standard deviation) in insect larvae in the Blackfoot River. Reference values are from Rock Creek, a tributary of the Clark Fork River unaffected by mine effluent. NC = not collected; NP = not present.

Kilometre	*Limnophilus*	*Brachycentrus*	*Arctopsyche*	*Hesperoperla*	*Claassenia*
211.8	NP	NP	NP	NP	NP
Beginning of masches					
207.3	1.8	NP	NP	NP	NP
200.5	NP	13.8	NP	0.64±0.16	0.69±0.30
End of masches					
190	0.56±0.14	2.3±1.4	2.6±0.08	1.04±0.62	0.52±0.17
186.6	0.42	0.54±0.07	0.42	1.00	
168–137	NP	0.37±0.21	0.07	0.27±0.12	0.24±0.04
74–87	NP	0.32±0.11	0.14	0.14±0.14	0.13±0.06
Reference	NP	NC	0.10±0.01		

TABLE 4. Cadmium, Cu, and Zn concentrations (μg/g dry weight ± 1 standard deviation) in the livers of trout from the upper Blackfoot River and a reference (Marshal Creek). All animals were 67 to 225 cm in length. The number of animals analyzed in one to six composites is shown in parentheses. NP = not present.

	Cd		Cu		Zn	
Kilometre	Brook	Cutthroat	Brook	Cutthroat	Brook	Cutthroat
211.8	18±13(6)	NP	1113±351(6)	NP	654±68(6)	NP
Beginning of marshes						
207.3	9.4±2.4 (25)	8.8 (2)	311±51(25)	24(2)	324±58(25)	135(2)
200.5	4.7±1.5(9)	5.9(3)	182±89(9)	34±18(3)	235±115(9)	146(3)
End of marshes						
190	0.70±0.26(7)	0.60±0.08(17)	135±57(7)	14±5(17)	138±12(7)	107±3(18)
186.6	<0.05(1)	0.17±0.06(16)	54(1)	13±5(16)	151(1)	106±1(16)
Reference	NP	0.18±0.07(18)	NP	15±6(18)	NP	103±3(18)

TABLE 5. Comparison of metal concentrations in livers of large brown trout (*Salmo trutta*), 341 to 475 cm in length, sampled in the middle reach of the Blackfoot River (near 123 and 134 km) with trout sampled below the confluence of the North Fork of the Blackfoot River at 74 km. * Significantly different from one another.

Kilometre	n	Cd	Cu	Zn
123–134	12	0.83±0.42*	846±398	111±10
74	6	0.07±0.05*	494±223	111±9

marsh system (Table 4). No significant differences in Zn concentrations occurred among stations in *Limnophilus* or *Claassenia*. The latter species may regulate Zn concentrations within their tissues.

Of the targeted species in this study, only brook trout (a depauperate population) were found upstream of the marsh system. Metal concentrations in the livers of the animals in this population suggested that substantial bioavailability of Cd, Zn, and Cu existed in conjunction with the high concentrations in the sediments and water. Metal concentrations in sediment and brook trout correlated strongly throughout the river, partly because of these upstream coincidences (r^2 = 0.971 for Cu, 0.922 for Zn, and 0.938 for log Cd). Zinc in brook trout was also correlated with Zn in water (r^2 = 0.984). Brook trout was the taxon in which the most obvious Cu contamination was observed (Table 4). The Cu concentration in the one brachycentrid composite from within the marsh was significantly ($p <$ 0.05), but only slightly, higher than observed at 190 km. No statistically significant differences occurred among any segments of the river below the marshes ($p > 0.05$) in insect larvae, cutthroat trout, or brown trout (Tables 4 and 6). Such results suggest that Cu was either of less widespread availability in the Blackfoot River than were Cd or Zn, or Cu was physiologically regulated by most of the species studied. Arsenic and Ni were somewhat variable, but neither element showed consistent enrichment in any species in any segment of the river. Both appeared to be of low bioavailability (data in Moore 1990).

Historic Comparisons of Fish Populations

Trout populations were recently studied in the Blackfoot River (Peters and Spoon 1989) because of an increase in complaints about dwindling numbers of fish. Selected data from that study, relevant to the determinations of metal distributions, are presented here and compared with surveys from the 1970's. The most striking results are from upstream. Eastern brook trout populations declined between 1971–73 and 1988 at three of four stations between 170 and 200 km; cutthroat trout populations declined at two of three relevant stations in this reach. Data from 200 km illustrate the magnitude of those changes and the differences in response between species and age classes (Fig. 6A and 6B).

The surveys of Spence (1975) were conducted first in 1973 and then again in 1975 following the failure of an abandoned tailings pond in the uppermost headwaters of the river (input at 214.6 km just below the largest source of mine effluent). "Young-of-the-year" brook trout (age 0) were present in 1973 at 200 km, but absent in 1975, suggesting acute mortalities

TABLE 6. Spatial distribution of Cu (μg/g dry weight ± 1 standard deviation) in insect larvae in the Blackfoot River. Reference values are from Rock Creek, a tributary of the Clark Fork River unaffected by mine affluent. NC = not collected; NP = not present.

Kilometre	*Limnophilus*	*Brachycentrus*	*Arctopsyche*	*Hesperoperla*	*Claassenia*
211.8	NP	NP	NP	NP	NP
Beginning of marshes					
207.3	27	NP	NP	NP	NP
200.5	NP	28.9	NP	32 ± 1	33 ± 6
End of marshes					
190	15 ± 2	17 ± 4	18 ± 1	23 ± 6	41 ± 5
186.6	27	16 ± 1	10	28	
168–137	NP	19 ± 3	15 ± 1	24 ± 3	42 ± 10
74–87	NP	16 ± 1	14 ± 4	29 ± 3	43 ± 8
Reference	NP	NC	12 ± 4	21	

from mine/milling wastes injected into the river by the pond failure (Fig. 6A). In 1988, age 0 brook trout populations had returned, but the fish were only 33% as abundant as in 1973. Age 1 (1 yr old) and older brook trout showed no apparent mortality from the pond failure; population densities were the same in 1973 and 1975. However, the effects of poor recruitment that would be expected from the reduced abundance of age 0 fish were evident in 1988. Age 1 and older brook trout populations were 72% lower in 1988 than during 1973–75, declining in average density downstream from 82/km to 23/km.

Age 0 cutthroat trout at 200 km also showed severe acute mortality in 1975; age 1 and older cutthroat were reduced in abundance (compare 1973 and 1975 in Fig. 6B). Age 0 cutthroat populations in 1988 remained severely reduced compared with 1973. In 1988, the abundance of age 1 and older cutthroat trout was less than 25% of that in 1973 and had declined by an additional 50% from 1975 (an 85% decline in cutthroat compared with 1975 was observed upstream at 207 km in 1988).

Differences between surveys also occurred in brown trout populations downstream from the most severe contamination. For example, at 170 km, significantly fewer age 1 brown trout and a possible downward trend in 2-yr-old plus older brown trout were observed from 1972 to 1988 (Fig. 6C). However, unlike trout populations in metal-affected areas, no decline in age 0 brown trout was evident.

Discussion

In the Blackfoot River, some solute and particulate contaminants extend downstream for 25 km from the major contaminant source, while others contaminate only a few kilometres of river immediately below inputs. Concentration of solute contaminants decreases rapidly in the upper few kilometres of input, probably related to the precipitation of Fe oxyhydroxides. As metal-rich mine effluent cascades down steep reaches of river, the entrainment of oxygen precipitates solute Fe and Mn (Michaelis 1988). The high concentration of sulfate also leads to the precipitation of metal sulfates (Nordstrom 1982). Other metals and metalloids can coprecipitate with or adsorb onto these sulfates and oxyhydroxides. This system of solute contaminant precipitation or adsorption works well in decreasing solute metal contaminants in the Blackfoot drainage above the marsh sytem but transfers metals to the particulate phase. Some solute and particulate contamination passes through the marsh system, and at least Cd and Zn remain bioavailable over long stretches of the river.

Within the marsh and downstream, Cd contamination is more severe than Zn and affected more species. Arsenic and Ni originating from acid mine drainage are of low bioavailability consistent with their relatively low concentrations in both the solute and particulate phases. Elevated solute Cu concentrations decrease to near limits of detection before entering the marsh system, which may partially explain their apparent limited availability to the biota. Although Cu is elevated in brook trout, the particulate Cu contamination that extends through the marsh system has no detectable effects on concentrations in other representatives from the food web.

Longer lived, predaceous species appeared to be more sensitive indicators of downstream Cd contamination than detritus feeding species and they were also better indicators than sediments or water. Significant Cd contamination was observed in stoneflies and large brown trout more than 75 km downstream from the input of acid mine drainage. Zinc was also significantly accumulated in some species in the middle reaches of the river. Thus, the order of downstream mobilization of bioavailable metals originating from the acid mine drainage appears to be Cd, Zn > Cu > As, Ni.

It is well established that natural marshes can improve water quality (Wolverton 1987) and that aquatic plants and bacteria can remove metals from acid mine drainage (Wolverton 1975; Wolverton and McDonald 1977). Natural and artificial marshes can decrease acidity, sulfate, and metal solute concentrations in acid mine drainage by 1 to 2 orders of magnitude (Huntsman et al. 1978; Wieder et al. 1982) by precipitation, adsorption, hydrolysis, redox and photochemical reactions, chelation, and filtration. The period of time over which marshes provide effective mitigation and the pathways that transfer contaminants from the mine effluent to the biota are poorly known. The Blackfoot River is typical of Rocky Mountain rivers contamined by abandoned mine drainage with a well-established beaver pond/marsh system that has received mine effluent for more than 100 yr. The Blackfoot example suggests that marsh systems may slow the transport of metals, but they do not necessarily completely stop downstream contamination of the food web by the most mobile of the metals. Particulate contaminants generally penetrated the marsh system to a greater extent than did solute contamination, but the marsh system is complex geochemically, possibly acting as both sink and source for different particulate metal contaminants.

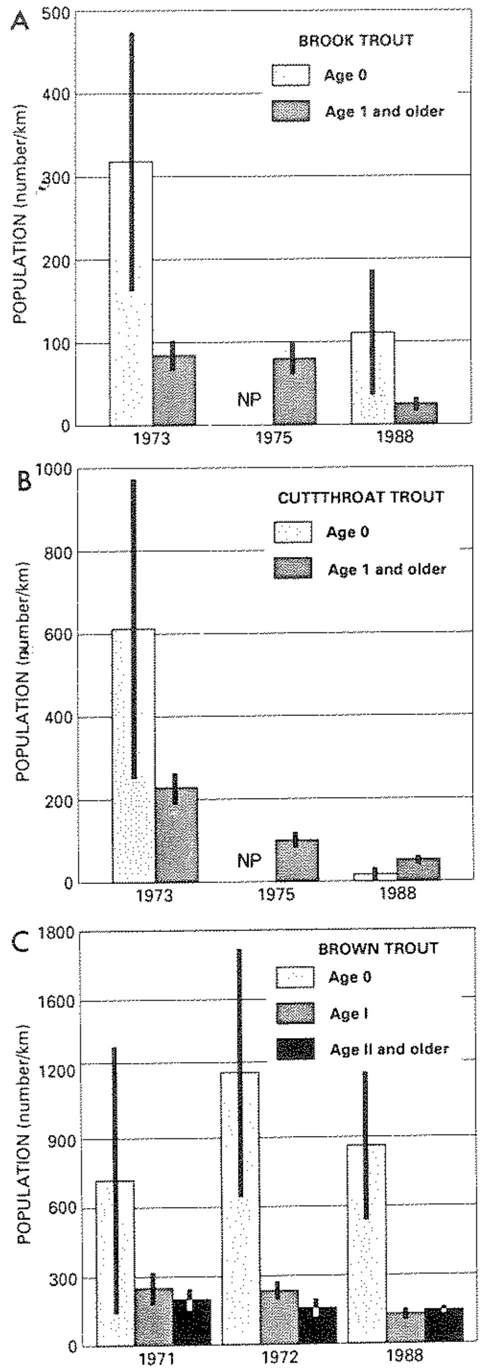

FIG. 6. Plots of population density of age 0 and age 1 plus older (A) brook trout and (B) cutthroat trout at 200 km in the Blackfoot River compared between the 1970's and 1988. (C) Brown trout population density at 170 km compared between the two sampling periods.

Other studies have shown that metals such as Cd, Pb, and Zn adversely affect both trout and their food web (Duncan and Klaverkamp 1982; Niederlehner et al. 1984; Hendrix et al. 1982; Selby et al. 1985; Harrison and Klaverkamp 1989; Schmitt and Finger 1987; Schmitt et al. 1984), although manifestation of such effects can be complex (Munkittrick and Dixon 1988; Schindler 1987). Adverse ecological effects of metals cannot be discounted in the Blackfoot River, where substantial contamination of sediment, water, and food webs from acid mine drainage is accompanied by depauperate benthic communities and fish populations. Surveys of the Blackfoot River conducted during low flow during 1968–71 (Spence 1975) also indicated a reduced number of bottom fauna species, especially mayflies, at 206.6 and 198.1 km but not at 192.6 or 186.5 km. The present study detected sediment contamination at 190 km and an absence of typical insect larvae (e.g. mayflies). This is a minimum data set, but it suggests that metal influences may extend further downstream than observed 16 yr earlier. Such changes may result from single large events or progressive change over decades, but are not detectable in consecutive years of sampling.

Before natural or artificial marshes are considered as long-term solutions for remedying continuous trace metal inputs from acid mine drainage, our study of the Blackfoot River suggests that a thorough study of particulate, aqueous, and biological components and consideration of long-term changes is necessary. If such systems typically fail to mitigate effects of upstream inputs of metals for an indefinite period, elimination of sources of metal input in such systems may be the most effective mechanism for preventing extended, long-term riverine contamination in Rocky Mountain riparian systems.

Acknowledgements

This work could not have been accomplished without the continuing contribution of ideas and enthusiasm from D. Cain and E. Axtmann plus the able field assistance of E. Axtmann, D. Cain, M. Cook, S. Andrews, V. Elrod, and D. Pridmore. Carolyn Johns originally suggested the idea of an integrated sediment–water–biota study on the Blackfoot and supplied laboratory and editorial assistance.

References

AXTMANN, E. V., D. J. CAIN, AND S. N. LUOMA. 1990. Distributions of trace metals in fine-grained, bed sediments and benthic insects in the Clark Fork River, Montana: Proceedings, Clark Fork River Symposium, Missoula, MT, April 20, 1989.

BOLLINGBERG, H. J., AND P. JOHANSEN. 1979. Lead in spotted wolffish, *Anarhichas minor*, near a zinc–lead mine in Greenland. J. Fish. Res. Board Can. 36: 1023–1028.

BRADLEY, S. B., AND J. J. COX. 1987. Heavy metals in the Hamps and Manifold Valleys, North Staffordshire, U.K.: partitioning of metals in floodplain soils. Sci. Total Environ. 65: 135–153.

BROOKS, R. R., J. R. LEWIS, AND R. D. REEVES. 1976. Mercury and other heavy metals in trout of Central North Island, New Zealand. J. Mar. Freshwater Res. 10: 233–244.

CAIN, D. J., J. L. CARTER, AND S. V. FEND. 1989. Temporal and spatial variability of arsenic in benthic insects from Whitewood Creek, South Dakota, *In* G. E. Mallard and S. E. Ragone [ed.] U.S. Geological Survey Toxics Substances Hydrology Program — Proceedings of the technical meeting, Phoenix, AZ, Sept. 26–30, 1988. U.S. Geol. Surv. Water Resour. Invest. Rep. 88-4220.

CHERNOFF, B., AND J. K. DOOLEY. 1979. Heavy metals in relation to the biology of the mummichog, *Fundulus heteroclitus*. J. Fish Biol. 14: 309–328.

DOLLHOPF, D. J., J. D. GOERING, R. B. RENNICK, R. B. MORTON, W. K. GAUGER, J. B. GUCKERT, P. M. JONES, K. C. COOKSEY, K. E. BUCKLIN, R. WEED, AND M. M. LEHMAN. 1988. Hydrochemical, vegetational and microbiological effects of a natural and a constructed wetland on the control of acid mine drainage. Montana Department of State Lands, Abandoned Mine Reclamation Bureau, Helena, MT, Reclamation Research Publication 88-04, June 1988. 214 p.

DUNCAN, D. A., AND J. F. KLAVERKAMP. 1982. Tolerance and resistance to cadmium in white suckers (*Catostomus commersoni*) previously exposed to cadmium, mercury, zinc, or selenium. Can. J. Fish. Aquat. Sci. 40: 128–138.

FILIPEK, L. H., D. K. NORDSTROM, AND W. H. FICKLIN. 1987. Interaction of acid mine drainage with waters and sediments of west Squaw Creek in the West Shasta Mining district, California. Environ. Sci. Tech. 21: 388–396.

GIESEY, J. P., J. W. BOLLING, H. J. KANIA, R. L. KNIGHT, AND S. MASHBURN. 1981. Fates of cadmium introduced into channels microcosm. Environ. Int. 5: 159–175.

Harrison, S. E., and J. F. Klaverkamp. 1989. Uptake, elimination and tissue distribution of dietary and aqueous cadmium by rainbow trout (*Salmo gairdneri* Richardson) and lake whitefish (*Coregonus clupeaformis* Mitchill). Environ. Toxicol. Chem. 8: 87–97.

Hendrix, P. E., C. L. Langner, and E. P. Odum. 1982. Cadmium in aquatic microcosms: implications for screening the ecological effects of toxic substances. Environ. Manage. 6: 543–553.

Huntsman, B. E., J. G. Solch, and M. D. Porter. 1978. Utilization of *Sphagnum* species dominated bog for coal acid mine drainage abatement. Geol. Soc. Am. Abstr. Program 10(7): 426.

Jones, K. C. 1986. The distribution and partitioning of silver and other heavy metals in sediments associated with an acid mine drainage stream. Environ. Pollut. 12B: 249–263.

Luoma, S. N., E. V. Axtmann, and E. J. Cain. 1989. Fate of mine wastes, Clark Fork River, Montana, U.S.A., p. 63–75. *In* Metals and metalloids in the hydrosphere; impact through mining and industry. Asian Inst. Tech. (UNESCO), Bangkok, Thailand.

Michaelis, H. V. 1988. Integrated biological systems for effluent treatment from mine and mill tailings, p. 99–112. *In* W. Solomons and U. Forstner [ed.] Environmental management of solid waste. Springer Verlag, New York, NY.

Moore, J. N. 1990. Mine effluent effects on non-point source contaminants in the Blackfoot River, Montana. Report to the Montana Department of Health and Environmental Sciences, Water Quality Bureau, Helena, Montana, May 1990. 64 p.

Moraiarity, F., K. R. Bull, H. M. Hanson, and P. Freestone. 1982. The distribution of lead, zinc and cadmium in sediments of an ore-enriched lotic ecosystem, the River Ecclesbourne, Derbyshire. Environ. Polzut. 4B: 45–68.

Munkittrick, K. R., and D. G. Dixon. 1988. Growth, fecundity, and energy stores of white sucker (*Catostomus commersoni*) from lakes containing elevated levels of copper and zinc. Can. J. Fish. Aquat. Sci. 45: 1355–1365.

Niederlehner, B. R., A. L. Buikema, Jr., C. A. Pittinger, and J. Cairns, Jr. 1984. Effects of cadmium on the population growth of a benthic invertebrate *Aeolosoma headleyi* (Oligochaeta). Environ. Toxicol. Chem. 3: 255–262.

Nordstrom, D. K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. Soil Sci. Soc. Am. Spec. Publ. 10: 37–56.

NOVA. 1990. Poison in the Rockies (transcript of video). WGBH-TV, Boston, MA. p. 2–3.

Peters, D., and R. Spoon. 1989. Preliminary fisheries inventory of the Big Blackfoot River. Montana Department of Fish, Wildlife and Parks, Missoula, MT. 46 p.

Ricker, W. F. 1975. Handbook of computations for biological statistics of fish populations. Fish. Res. Board Can. Bull. 119: 300 p.

Roch, M., J. A. McCarter, A. T. Matheson, M. R. Clark, and R. W. Olafson. 1982. Hepatic metallothionein in rainbow trout (*Salmo gairdneri*) as an indicator of metal pollution in the Campbell River system. Can. J. Fish. Aquat. Sci. 39: 1596–1601.

Schindler, D. W. 1987. Detecting ecosystem responses to anthropogenic stress. Can. J. Fish. Aquat. Sci. 44(Suppl. 1): 6–25.

Schmitt, C. J., F. J. Dwyer, and S. E. Finger. 1984. Bioavailability of Pb and Zn from mine tailings as indicated by erythrocyte δ-aminolevulinic acid dehydratase (ALA-D) activity in suckers (Pisces: Catastomidae). Can. J. Fish. Aquat. Sci. 41: 1030–1040.

Schmitt, C. J., and S. E. Finger. 1987. Effects of sample preparation on measured concentrations of eight elements in edible tissues of fish from streams contaminated by Pb mining. Arch. Environ. Contam. Toxicol. 16: 185–207.

Selby, D. A., J. M. Ihnat, and J. J. Messer. 1985. Effects of subacute cadmium exposure on a hardwater mountain stream microcosm. Water Res. 19: 646–655.

Spence, L. E. 1975. Upper Blackfoot River — A preliminary inventory of aquatic and wildlife resources. Montana Department of Fish and Game, Missoula, MT. 236 p.

Wieder, R. K., G. E. Lang, and A. E. Whitehouse. 1982. Modification of acid mine drainage in a fresh water wetland, p. 38–62. *In* Proceedings, Acid Mine Drainage Research and Development, West Virginia Surface Mine Drainage Task Force Symposium, Charleston, WV.

Wiener, J. G., and J. P. Giesy, Jr. 1979. Concentrations of Cd, Cu, Mn, Pb, and Zn in fishes in a highly organic softwater pond. J. Fish. Res. Board Can. 36: 270–279.

Winner, R. W., M. W. Boesel, and M. P. Farrell. 1980. Insect community structure as an index of heavy-metal pollution in lotic ecosystems. Can. J. Fish. Aquat. Sci. 37: 647–655.

Wolverton, B. C. 1975. Water hyacinths for removal of cadmium and nickel from polluted waters. NASA Tech. Memo. TM-X-72721.

1987. Artificial marshes for wastewater treatment, p. 141–152. *In* K. R. Reddy and W. H. Smith [ed.] Aquatic plants for water treatment and resource recovery. Magnolia Publ. Inc., Orlando, FL.

Wolverton, B. C., and R. C. McDonald. 1977. Wastewater treatment utilizing water hyacinths (*Eichhornia crassipes*) (Mart) Solms, p. 205–208. *In* Treatment and disposal of industrial wastewaters and residues. Proceedings of National Conference, Houston, TX.